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(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
26 July 2001 (26.07.2001)

PCT

(10) International Publication Number  
**WO 01/54216 A2**

- (51) International Patent Classification: **H01M 8/00** (74) Agent: **REINHOLD COHN AND PARTNERS; P.O. Box 4060, 61040 Tel Aviv (IL).**
- (21) International Application Number: **PCT/IL01/00055**
- (22) International Filing Date: **18 January 2001 (18.01.2001)** (81) Designated States (national): **AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.**
- (25) Filing Language: **English**
- (26) Publication Language: **English**
- (30) Priority Data:  
09/484,267 18 January 2000 (18.01.2000) US  
09/604,297 26 June 2000 (26.06.2000) US
- (71) Applicant (for all designated States except US): **RAMOT UNIVERSITY AUTHORITY FOR APPLIED RESEARCH AND INDUSTRIAL DEVELOPMENT LTD. (IL/IL); P.O. Box 39296, 61392 Tel Aviv (IL).**
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): **PELED, Emanuel (IL/IL); 25 Hanotea Street, 40500 Even Yehoda (IL). DU-VDEVANI, Talr (IL/IL); 19 Carmeli Street, 52233 Ramat Gan (IL). MELMAN, Avi (IL/IL); 30 Kdoshei Kahir Street, 58362 Holon (IL). AHARON, Adi (IL/IL); 57 Hagagana Street, 46325 Herzliya (IL).**
- (84) Designated States (regional): **ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).**

**Published:**

— without international search report and to be republished upon receipt of that report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 01/54216 A2

(54) Title: **FUEL CELL WITH PROTON CONDUCTING MEMBRANE**

(57) Abstract: The present invention provides improved, low-cost fuel cells having reduced fuel crossover, reduced sensitivity to metal ion impurities and ability to operate under a broad range of temperatures. The invention further provides improved methods for catalyst preparation and a new integrated flow field system for use in H<sub>2</sub>/O<sub>2</sub> fuel cells.

## FUEL CELL WITH PROTON CONDUCTING MEMBRANE

### FIELD OF THE INVENTION

This invention relates to an electric cell that converts the chemical energy obtained in a fuel oxidation reaction directly into electric energy in a continuous process. More specifically the invention relates to fuel cells.

### 5 BACKGROUND OF THE INVENTION

Fuel cells are often described as continuously operating batteries or as electrochemical engines. Fuel cells utilize an external supply of fuel and oxygen (or air) and produce power continuously, as long as the fuel and oxygen supply is maintained.

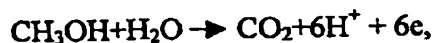
10 The most classic fuel cell is the  $H_2/O_2$  fuel cell of the direct or indirect type, wherein hydrogen is oxidized to form  $H_3O^+$  at the anode and oxygen is reduced to water at the cathode. In the direct type, hydrogen and oxygen are used as such, the fuel being produced in independent installations. The indirect type employs a hydrogen-generating unit, which can use as raw material a wide variety of fuels.

15 Another type of fuel cell is the organic fuel cell. In a direct oxidation cell an aqueous solution of an organic fuel such as methanol, formaldehyde or formic acid, is directly fed into the fuel cell without any previous chemical modification, where the fuel is oxidized at the anode, and oxygen is reduced to water at the cathode.

- 2 -

A major distinguishing characteristic of different fuel cells is in the electrolyte used. NASA's Jet Propulsion Laboratory (JPL) developed a direct liquid-feed cell using a solid membrane electrolyte. A detailed description of JPL's fuel cells can be found, for example, in U.S. Patent Nos. 5,599,638 and 5,773,162.

5 These fuel cells operate without any acid electrolyte and comprise solid electrolyte membranes fabricated from proton-exchange materials, especially Nafion™ (manufactured by DuPont). When methanol is used as the fuel, the electro-oxidation of methanol at the anode can be represented by:



10 and the electro-reduction of oxygen at the cathode can be represented by :



Protons generated at the anode are transported directly across the electrolyte membrane to the cathode. A flow of current is sustained by a flow of ions through the cell and electrons through the external load.

15

## SUMMARY OF THE INVENTION

The challenge in fuel cell development for practical applications is to improve the economics through the use of low-cost components with acceptable

20 life and performance.

Thus, the present invention provides by the first of its aspects a fuel cell comprising an anode chamber including an anode and means for providing fuel to the anode, a cathode chamber including a cathode and means for providing oxygen to the cathode, and a solid electrolyte membrane disposed between said cathode

25 and said anode, wherein said solid electrolyte membrane is a proton conducting membrane having pores with a diameter, smaller than 30 nm, said membrane comprising:

- 3 -

- (i) 5% to 60% by volume, preferably 8% to 30% by volume of an electrically nonconductive inorganic powder having a good acid absorption capacity, said powder comprising nanosize particles;
- (ii) 10% to 90% by volume, preferably 30% to 80% by volume of an acid or aqueous acid solution; and
- (iii) 5% to 50% by volume, preferably 12% to 40% by volume of a polymeric binder that is chemically compatible with said acid, oxygen and said fuel.

Typically, when the fuel used is organic, it is provided as a fuel aqueous solution.

The solid proton conducting membrane used in the fuel cells of the present invention has been described in WO 99/44245. The polymeric binders used in these membranes may be selected from the group consisting of poly(vinylidenefluoride), poly(vinylidenefluoride)hexafluoropropylene, poly(tetrafluoroethylene), poly(methyl methacrylate), poly(sulfoneamide), poly(acrylamide), poly(vinylchloride), acrylonitrile, poly(vinylfluoride), Kel F<sup>TM</sup> and any combinations thereof.

The inorganic nanosize powder used for preparing the solid proton conducting membrane may be selected from the group consisting of SiO<sub>2</sub>, ZrO<sub>2</sub>, B<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, hydroxides and oxy- hydroxydes of Ti, Al, B and Zr, and any combinations thereof.

As described above, the proton conducting membrane used in the fuel cell of the invention comprises, *inter alia*, an acid. Typically, the diameter of the membrane pores is smaller than 30nm, preferably smaller than 3 nm, more preferably smaller than 1.5 nm. As opposed to the solid electrolyte membrane described for example in U.S. Patent No. 5,599,638, wherein no acid is present in free form, the solid electrolyte membrane used in the fuel cell of present invention contains free acid molecules entrapped in the pores of the membrane. Alternatively, it may contain acid molecules bonded to the inorganic powder.

Thus, such a PCM comprises a matrix made of silica powder, preferably nanopowder, bonded with an appropriate polymer binder described above, and

- 4 -

acid molecules chemically bonded to the silica, thus reducing or avoiding the need to insert acid into the fuel solution. Other nanopowders can be used in a similar way. According to this option the acid, preferably sulfonic acid, is chemically bonded to the inorganic nanopowder directly or through an organic segment R selected from  $-(CH_2)_n-$ ,  $-(CF_2)_n-$ ,  $-(CF_2CH_2)_m-$ , where n is an integer from 1 to 10 and m is an integer from 1 to 5, perfluoroaryl, polyfluoroaryl, perfluorostyrene, polyfluorostyrene and similar segments where up to 50 % of the hydrogen or fluorine atoms were replaced by chlorine atoms.

A non limiting procedure to form sulfonic acid groups bonded to silica is described hereinbelow: nano size silica powder is boiled in pure water for two hours to enrich the powder surface with OH groups. Then the hydrated powder is immersed in a solution of chloro, methoxy, or alkoxy organo sulfur silan of the type  $CH_3COSR-Si(OCH_3)_3$  or  $CH_3COSR-SiCl_3$ , where R is one of the organic segments listed above. The silan reacts with the surface OH groups of the silica powder to form up to one monolayer of the organic sulfur silan. Then the powder is oxidized by air and the thioacetat group is converted into a sulfonic acid group. This step is described in the following equation:



The obtained chemically bonded sulfonic acid is stable in strong acids at 90 °C and, therefore, it may be used in the preparation of a PCM for fuel cell applications, instead of pristine  $SiO_2$ .

The anode and the cathode comprise a catalyst layer and optionally also a porous backing layer. A preferred catalyst used at the anode is for example nano size platinum-ruthenium powder, while preferred catalysts used at the cathode are for example nano size platinum powder and alloys thereof with non noble metals, for example Ni, Co, and Fe. In such alloys the ratio between platinum and the metal (Pt:M atomic ratio) is between about 1:3 to about 3:1.

A large variety of low vapor pressure acids that are compatible with the cell hardware and with the catalysts at both electrodes may be used in accordance with the invention.

- 5 -

The backing layer is preferably made of carbon. This layer is porous and is used for support and at the same time for making electrical contact between the housing and the catalyst powder, which by itself is connected to the membrane.

The means for circulating an fuel past the anode and for flowing oxygen or  
5 air past the cathode include also means for withdrawing carbon dioxide, unused fuel and water from the anode side and for withdrawing unused oxygen and water from the cathode side.

One advantage of the fuel cell according to the invention over current art fuel cells is that it uses a membrane that is easily wet. Thus, there is no need to  
10 develop special means for membrane humidification, as is the case in current art fuel cells, as evident, for instance, from US 5,952,119 to Wilson, which states that "one of the primary challenges in attaining optimal performance of polymer electrolyte membrane fuel cell is attaining effective hydration of the ionomeric membrane structure". Wilson suggests solving this problem by applying a  
15 hydrophilic wick to wick liquid water to the membrane. As the fuel cell of the present invention does not show wetting difficulties, such a wick is saved, and the cell construction is simplified.

According to one embodiment of the present invention, the fuel cell of the invention is a  $H_2/O_2$  fuel cell, wherein two sets of integrated flow channels are  
20 engraved in the cathode chamber or in the anode chamber. In one set of channels of this embodiment reactant gases are flowing, and in the other - the electrolyte is circulating.

According to yet another aspect of the present invention there is provided a method for reconditioning a direct oxidation fuel cell, the method comprises the  
25 steps of:

(a) operating the cell at a reversed voltage of 0.6 to 1.3V for a period of time T.

Preferably, the time period T is between 1 to 100 minutes. A longer period T is preferable as the cell ages or as it suffers a higher level of impurities.

30 Preferably, the voltage is between 0.6 and 1.3V.

- 6 -

The inventors applied this reconditioning procedure 10 times, each time for 1 to 30 minutes, during a 3500 hours operating period of a fuel cell and found an improvement of the cell voltage of 50 to 100mV.

The invention also provides a method for preparing a catalyst layer for use in a fuel cell, said method comprising the steps of forming up to one monolayer of a catalyst on the surface of a nanosize inorganic powder, such monolayer serving as a nucleation site, forming additional one or more catalyst layers on the top of said first monolayer to obtain catalyst particles and subsequently binding the obtained particles to the carbon backing layer and/or to the proton conducting membrane.

According to another aspect of the present invention there is provided a hybrid power source comprising a liquid feed fuel cell according to the invention, a DC to DC converter and a rechargeable battery.

According to another aspect of the present invention there is provided a device for controlling the water return flow from the cathode side to the anode side in a fuel cell, comprising a water or fuel solution level sensor and air or oxygen pressure control unit placed in the cathode compartment, and a fuel cell comprising such a device.

According to another aspect of the present invention there is provided a method for reducing crossover current in a fuel cell having an anode chamber with an anode and a fuel tank for providing said anode with fuel, a cathode chamber with a cathode and means for providing said cathode with oxygen in a given pressure, a solid electrolyte membrane disposed between said cathode and said anode, and a tank for water or fuel solution, an air or oxygen pressure control unit and a sensor for sensing the level fuel solution in said fuel tank and means for controlling said pressure in response to said level of water or fuel, comprising the steps of:

- (a) sensing the level of the water or fuel in the water or fuel tank;
- (b) controlling the air or oxygen gas pressure in the cathode chamber to increase as the level of water or fuel solution sensed in step (a)

- 7 -

decreases;

thus reducing the crossover current.

According to another aspect of the present invention there is provided a free direct oxidation fuel cell having a low crossover current density, wherein the fuel solution tank is directly attached to the anode chamber, the fuel concentration is between 1% and 40% (w/w) and the ratio between the tank volume (in ml) and the electrode area, in  $\text{cm}^2$  is between 3:1 and 30:1.

According to another aspect of the present invention there is provided an orientation independent direct oxidation fuel cell system having

- 10 (a) an anode chamber with an anode, fuel inlet and gas outlet;
- (b) a cathode chamber with a cathode and oxygen or air inlet;
- (c) an electrolyte membrane disposed between the anode and the cathode;
- and
- (d) a fuel tank connected to the anode chamber,

15 wherein

- i) said fuel tank being divided by a movable barrier into two parts,  
said first part of the fuel tank being capable of containing  
fuel or fuel solution and connected to the anode chamber,  
said second part of the fuel tank holding gas with pressure  
20 greater than atmospheric pressure or having a closable gas  
inlet;

- ii) said gas outlet being closed with a gas permeable hydrophobic  
matrix;

said barrier being capable of directing fuel or fuel solution from the  
25 fuel tank to the anode chamber irrespective of the fuel cell orientation.



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